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In the production of structures made from reinforced cyanate ester resins, nearly complete cyclotrimerization of the resin with concomitant macromolecular network formation must be achieved in order to ensure adequate mechanical performance and durability of the structures. In the course of developing a wide variety of new cyanate ester resins, as well as in studies of co-cured blends, it has become apparent that some resins can be fully cured into robust networks quite readily under benign conditions, even with a very limited degree of catalysis. Others, though, require post-cure at such high temperatures that the resin undergoes thermochemical degradation during the cure process, while still others are unable to achieve a high degree of cure or form a macromolecular network under any known conditions. Because of the highly selective nature of cyanate ester cyclotrimerization, these differences provide an exceptional opportunity to study the influence of the molecular structure of the monomer on the ability to form a fully cured network structure. For dicyanates of the bisphenol type in particular, studies of cure kinetics and network formation employing differential scanning calorimetry, infrared spectroscopy, and thermomechanical analysis have helped to illuminate important aspects of the links among molecular rigidity, molecular topology, thermal activation, and network formation.

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THE INFLUENCE OF MONOMER CHEMICAL STRUCTURE ON LATE-STAGE CURE KINETICS OF DICYANATE ESTER RESINS

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ABSTRACT

In the production of structures made from reinforced cyanate ester resins, nearly complete cyclotrimerization of the resin with concomitant macromolecular network formation must be achieved in order to ensure adequate mechanical performance and durability of the structures. In the course of developing a wide variety of new cyanate ester resins, as well as in studies of co-cured blends, it has become apparent that some resins can be fully cured into robust networks quite readily under benign conditions, even with a very limited degree of catalysis. Others, though, require post-cure at such high temperatures that the resin undergoes thermochemical degradation during the cure process, while still others are unable to achieve a high degree of cure or form a macromolecular network under any known conditions. Because of the highly selective nature of cyanate ester cyclotrimerization, these differences provide an exceptional opportunity to study the influence of the molecular structure of the monomer on the ability to form a fully cured network structure. For dicyanates of the bisphenol type in particular, studies of cure kinetics and network formation employing differential scanning calorimetry, infrared spectroscopy, and thermomechanical analysis have helped to illuminate important aspects of the links among molecular rigidity, molecular topology, thermal activation, and network formation.

1. INTRODUCTION

Cyanate ester resins [1-3] are an important emerging class of thermosetting polymers that have been candidates for use in a wide variety of applications, ranging from micro-capacitors [4] to insulation for thermonuclear fusion reactors [5] to interplanetary space probes [6]. Cyanate esters offer ease of processing through methods such as pultrusion [7], filament winding [8], and VARTM [9], with higher maximum use temperatures, better flame, smoke, and toxicity characteristics, and lower health and safety risks during handling when compared to epoxy resins [10]. Cyanate esters also offer generally lower water uptake and exceptionally low coefficients of hygrothermal expansion [11] for thermosetting polymers.

Understanding the cure kinetics of cyanate ester resins is perhaps the most important factor in successfully developing successful part production techniques. Although much effort has focused on describing the effects of catalysts (including moisture) on cyanate ester cure reactions [12-18], an important aspect of the cure process that has received relatively less attention [19] is the post-vitrification behavior. Like all thermosetting resins, cyanate esters first pass through a

gel point followed by vitrification during cure, at which point the cure reaction slows down greatly. As a result, a cyanate ester part will spend most of its production time in the post-vitrification stage, where the production process target is typically the attainment of a consistent conversion close to 100%.

Although superficially, small differences in conversion near 100% may not seem particularly important, several features of cyanate ester resins make the physical properties of interest quite sensitive to the degree of conversion, even near 100%. For example, dicyanate ester resins tend to follow the diBenedetto equation [20] relating conversion to dry glass transition temperature (T_g) quite closely. The diBenedetto equation describes an increasing sensitivity of T_g to conversion as conversion approaches 100%, with the magnitude of the sensitivity determined by the difference between uncured and fully cured T_g. Cyanate esters are noted for the unusually large difference between monomer T_g (around -50 °C) and fully cured T_g (around 300 °C). As a result, the T_g for a cyanate ester resin at nearly complete conversion can vary by 7-8 °C for every 1% change in conversion [11]. In addition, cyanate ester resins show significant increases in free volume as conversion approaches 100%, affecting everything from elastic modulus [21] to water uptake [11]. Finally, the presence of unconverted cyanate ester groups and water at high temperatures has been shown to lead to chemical reactions that produce significant quantities of volatiles [22], leading to blisters and voids in finished parts.

In what follows, the late stage cure kinetics and resultant physical properties are compared for three different dicyanate ester resins catalyzed by transition metals in combination with nonylphenol. Although the three resins have quite similar chemical structures, differences in rigidity appear to cause significant differences in late stage cure kinetics, despite indications of similar levels of catalysis from differential scanning calorimetry (DSC) measurements. Moreover, the degree of conversion ultimately obtained is particularly sensitive to final cure temperatures. Key physical properties of the resins, such as moisture uptake, are also significantly affected by relatively modest differences in the degree of conversion. These results have significant implications for efforts to produce cyanate ester components with optimal physical properties through economically advantageous processing schedules.

2. EXPERIMENTATION

2.1 Materials

The dicyanate esters of Bisphenol A (Primaset® BADCy) and Bisphenol E (Primaset® LECy) were purchased from Lonza and used as received. “SiMCy”, a silicon-containing analog of Primaset® BADCy, was synthesized according to the procedure specified in the literature [23]. Nonylphenol (technical grade) was purchased from Aldrich, and Copper (II) acetylacetonate was purchased from ROC/RIC; both were used as received.

2.2 Sample Preparation

Batches of catalyst comprised of 30 parts by weight nonylphenol to one part by weight of copper (II) acetylacetonate were prepared by mixing the ingredients in a vial and heating to 60°C while stirring vigorously until complete dissolution took place (typically one to two hours). These batches were retained for up to 30 days. Due to the low humidity ambient environment, the only precautions taken when storing the Primaset® BADCy and LECy resins were the use of tightly sealed containers and avoidance of exposure to high humidity environments. However, for the novel material SiMCy, for which the stability data are unknown, the sample was stored at or below 4°C as an added precaution.

Uncured samples for differential scanning calorimetry (DSC) analysis were prepared by mixing monomer with 2 parts per hundred by weight of catalyst at 95°C, following which the mixture was partially de-gassed at 95 °C for 30 minutes under reduced pressure (300 mm Hg). To

prepare cured samples, silicone molds made from R2364A silicone from Silpak Inc. (mixed at 10:1 by weight with R2364B platinum-based curing agent and cured overnight at room temperature, followed by post-cure at 150°C for 1 hour) were prepared by de-gassing for 60 minutes at 95°C and 300 mm Hg. The uncured cyanate ester mixture was mixed and de-gassed using the method for preparing DSC samples described above, and then poured into the prepared mold (no release agent was used). The open mold and sample were then placed under flowing nitrogen at 25°C and ramped 5°C/min to the corresponding cure temperature and held at that temperature for 12 hours to produce void-free discs measuring approximately 11.5-13.5 mm in diameter by 1-3 mm thick and weighing 200-400 mg. BADCy samples with a final cure temperature of 200°C were first brought to 150°C for 1 hour before being ramped to 200°C, in order to avoid excess vaporization of monomer. The discs were used for thermomechanical analysis (TMA), and hot water exposure tests.

2.3 Characterization Techniques

DSC was performed on a TA Instruments Q2000 calorimeter under 50 mL/min. of flowing nitrogen. Samples were heated to their respective cure temperatures for 12 hours and then cooled to 0°C at 20°C/min. The samples were then heated to 350 °C, then cooled to 25 °C and re-heated to 350 °C, all at 10 °C/min. Oscillatory TMA was conducted with a TA Instruments Q400 series analyzer under 50 mL/min of nitrogen flow. The discs were held in place via a 0.2 N initial compressive force with the standard ~5 mm diameter flat cylindrical probe while the probe force was modulated at 0.05 Hz over an amplitude of 0.1 N (with a mean compressive force of 0.1 N) and the temperature was ramped to 350°C followed by two heating and cooling cycles between 100 °C and 200 °C (to determine thermal lag), all at 20 °C/min. Fourier Transform Infrared Spectroscopy (FT-IR) was carried out using a Thermo Corporation Nicolet 6700 FT-IR Spectrometer in attenuated total reflectance mode with a resolution of 4 cm^{-1}. Spectra were collected by averaging 32 scans.

3. RESULTS

Three different dicyanate esters, Primaset® LECy, Primaset® BADCy, and SiMCy, were used for late stage cure kinetic studies and their structures are shown in Figure 1. The monomers were brought to different degrees of cure by heating the monomers at different temperatures for 12 hours. Based on the results of DSC experiments, cure temperatures were selected that gave approximate conversions (that is, extents of cure) of 0.7, 0.8 and 0.9 for each material. Cure temperatures of 125 °C, 150 °C and 200 °C were chosen for BADCy; 125 °C, 150 °C and 170 °C for LECy; and 100 °C, 125 °C and 150 °C for SiMCy. All samples were cured for 12 hours at the indicated cure temperature.

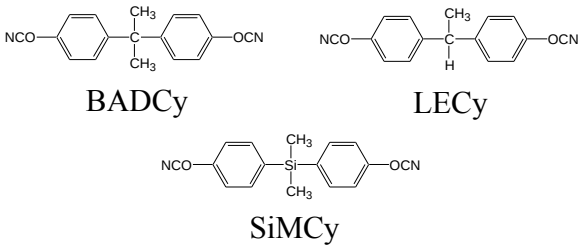


Figure 1. Chemical structures of the cyanate ester monomers studied.

3.1 Determination of Extent of Cure

To determine the extent of cure, dicyanate monomers were cured isothermally in a DSC instrument for 12 hours at a given temperature, then cooled to 0 °C at 20 °C/min and heated to 350 °C at 10 °C/min. During this heating cycle the cyclotrimerization exotherm of unreacted cyanate groups was used to determine the extent of cure using the equation

$$\chi = \frac{(\Delta H_0 - \Delta H)}{\Delta H_0} \qquad [1]$$

where ΔH_0 is the enthalpy of cyclotrimerization of the uncured monomer and ΔH is the residual enthalpy of cure for the partially cured material. In accordance with the trends in equivalent weight and the highly similar enthalpy of cure (on a molar equivalent basis) for cyanate ester groups, the enthalpy of cyclotrimerization of LECy dicyanate was the highest of the three materials, followed by BADCy then SiMCy (Table 1). In fact, on a molar equivalent basis, the enthalpy of cure was 102 kJ/eq. for LECy and 98 kJ/eq. for both BADCy and SiMCy, very close to the generally accepted average of 100 kJ/eq. [2], although slightly higher than the 83-95 kJ/eq. previously reported]24] for these catalyzed monomers.

Table 1. Enthalpies of cyclotrimerization for pure dicyanate monomers and residual cyclotrimerization enthalpies for cyanates cured for 12 hours.

Monomer	Cure Temp. (°C)	ΔH (J/g)	ΔH_0 (J/g)
BADCy	Not cured	-	700
LECy	Not cured	-	770
SiMCy	Not cured	-	670
BADCy	125	180	-
BADCy	150	140	-
BADCy	200	60	-
LECy	125	190	-
LECy	150	110	-
LECy	170	70	-
SiMCy	100	150	-
SiMCy	125	100	-
SiMCy	150	50	-

The extent of cure (conversion) values for partially cured BADCy, LECy and SiMCy were calculated using Equation 1 and are listed in Table 2. The temperatures required for each material to reach the targeted extents of cure varied significantly. To attain 90 percent conversion, as determined by DSC, BADCy required a cure temperature of 200 °C, whereas SiMCy needed a cure temperature of only 150 °C to reach a similar degree of cure. It was found

that the cure temperature, not time, was the primary factor that determined the particular extent of cure. Experiments in which the cure time was varied from 1 hour to 24 hours resulted in only a small change in the extent of cure.

Table 2. Extent of cure determined by residual cure enthalpy for samples cured in a DSC instrument for 12 hours.

Final Cure Temperature (°C)	**Extent of Cure**		
	BADCy	**LECy**	**SiMCy**
100	-	-	0.77
125	0.74	0.75	0.85
150	0.80	0.86	0.93
170	-	0.91	-
200	0.92	-	-

The extent of cure was qualitatively confirmed by IR spectroscopy. The cyanate ester C≡N stretch occurs at 2200-2300 cm^{-1} and absorbs as a doublet characteristic of aryl cyanate esters. This absorption is known to decrease with increasing conversion of cyanate ester groups to triazine rings. A stacked plot of IR spectra for BADCy cured at different temperatures is shown in Figure 2. As the cure temperature of BADCy samples was increased, the C≡N stretch at 2236 cm^{-1} and 2270 cm^{-1} absorption band decreased. The IR spectra for the LECy and SiMCy materials also showed the same decrease in cyanate ester absorption bands with increase in conversion. The relative sizes of the C≡N stretch band compared to reference bands at 2800 - 3000 cm^{-1} (aliphatic C-H stretch) and 1500 cm^{-1} (phenyl ring), though not a quantitatively accurate measure of conversion, were qualitatively consistent with the extent of cure values determined via DSC.

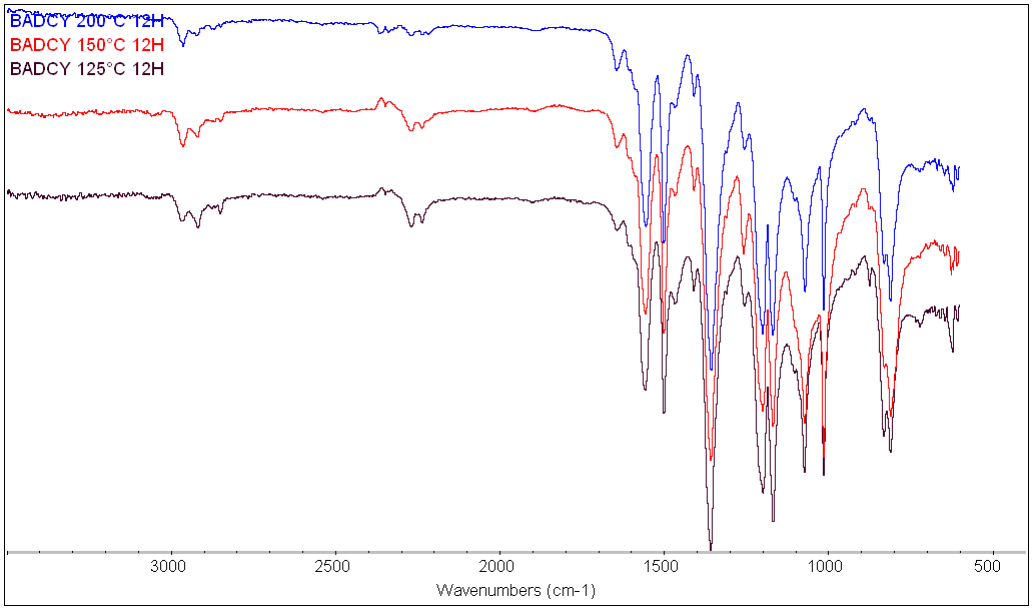


Figure 2. IR spectra of BADCy cured at different temperatures.

The temperatures required to reach a particular degree of conversion reflect the relative "ease" of cure for the different monomers and follow the trend SiMCy > LECy > BADCy. This is somewhat surprising given the similarity in molecular structure of the monomers and the similar peak cure exotherm temperatures and enthalpies of cyclotrimerization. On the other hand, if the cyanate ester monomers are viewed as consisting of aryl cyanate arms attached to a "core" of variable molecular bond flexibility, then the SiMCy monomer would be expected to exhibit the greatest core flexibility, due to the longer Si-C bonds that feature a lower deformation energy, followed by the LECy, which is somewhat more flexible than the BADCy due to lower steric hindrance around the core bonds. The relative core flexibilities are reflected in the fully cured T_g values for the monomers, which increase in the order SiMCy (274 °C), LECy (291 °C), BADCy (298 °C) [24]. When viewed from the standpoint of core flexibility, the most flexible core corresponds to the greatest ease of cure, a result previously observed for tricyanate esters [25] as well.

The glass transition temperature was also used to determine the extent of cure of cyanate esters as a function of cure temperature. The T_g of polycyanurate systems has been shown to follow a unique relationship with the extent of conversion (χ) and is accurately described by the diBenedetto equation [20] (Equation 2).

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda\chi}{1-(1-\lambda)\chi} \qquad [2]$$

T_{g0} and $T_{g\infty}$ are the monomer T_g and the T_g of the fully cured material respectively and were determined by DSC. A value of 0.6 was used for the experimental parameter λ in accord with previous determinations for polycyanurate systems [26].

The glass transition temperature of cyanate ester monomers cured in a DSC instrument for 12 hours was measured by heating the sample at a ramp rate of 10°C/min after the sample had been cured in the DSC instrument. In most cases the sample had vitrified, i.e. the T_g was higher than the cure temperature, and the T_g relaxation was immediately followed by the cyclotrimerization exotherm of unreacted cyanate groups. The T_g of polycyanurate disks cured in an oven were measured using oscillatory TMA. The glass transition was determined from the loss modulus peak temperature after correcting for thermal lag. The glass transition temperatures determined by DSC and TMA methods and the resulting extents of cure calculated using the diBenedetto equation are summarized in Table 2. The T_g's, and therefore the extents of cure, determined by the two different methods agree well with each other.

The extents of cure measured by the residual enthalpy of cure were higher than the extents of cure calculated from the diBenedetto equation for all materials. Given the relative error inherent in DSC measurements (due to uncertainties in the sample weight, which are generally random, and uncertainties in the baseline, which tend to be systematic), the discrepancies were generally within expectations, exceeding a conversion difference of 0.07 only in one case.

The discrepancies, however, do appear somewhat larger for SiMCy than for the other two monomers. In the case where a large discrepancy exists, partial cure of the sample may have been the cause. All samples were first de-gassed at 95°C for 30 minutes before a portion of the monomer / catalyst mixture was used for DSC analysis; during this time a small amount of the monomer may have cured resulting in a low ΔH value and a higher than actual calculated extent of cure. Due to their relative "ease" of curing, the SiMCy samples would be more likely affected by occasional unintended cure, with the least cured sample (with a cure temperature only 5 °C higher than the de-gassing temperature) the most likely to be affected. Another explanation for the systematic differences would be an incorrect value for the λ parameter in the diBenedetto equation, though a fairly low value of 0.4 – 0.45 would be needed to make the results coincide.

Table 2. T_g and extent of cure of BADCy LECy and SiMCy cured at different temperatures.

Sample ID[a]	T_g (°C) DSC	$\chi_{(DSC)}$[b]	T_g (°C) OTMA[c]	$\chi_{(OTMA)}$	$\chi_{(DSC)}$[d]
BADCy 125	134	0.66	147	0.69	0.74
BADCy 150	168	0.74	169	0.74	0.80
BADCy 200	246	0.90	248	0.91	0.92
LECy 125	142	0.69	147	0.70	0.75
LECy 150	183	0.79	188	0.80	0.86
LECy 170	213	0.86	213	0.86	0.91
SiMCy 100	91	0.56	105	0.60	0.77
SiMCy 125	152	0.73	168	0.78	0.85
SiMCy 150	186	0.82	203	0.86	0.93

[a]Sample ID consists of the monomer name followed by the cure temperature in °C; cure times were 12 hrs
[b]Determined from the diBenedetto equation with λ=0.6
[c]Determined from the peak of the loss modulus after thermal lag correction.
[d]Determined from residual cyclotrimerization enthalpy

The relative ease of cure of the SiMCy dicyanate monomer is illustrated in the T_g versus cure temperature plot for the three different monomers studied (Figure 3). Despite having the lowest fully cured T_g of the three monomers, the SiMCy dicyanate generally had the highest T_g for a given cure temperature while BADCy (having the highest fully cured T_g) displayed the lowest T_g for a given cure temperature. For example, when cured at 150°C for 12 hours, SiMCy reached a T_g approximately 30°C higher than BADCy. The ease of cure of SiMCy makes it a potentially useful cyanate resin in applications where the cure temperature is limited yet the highest attainable T_g, and therefore maximum use temperature, is desired.

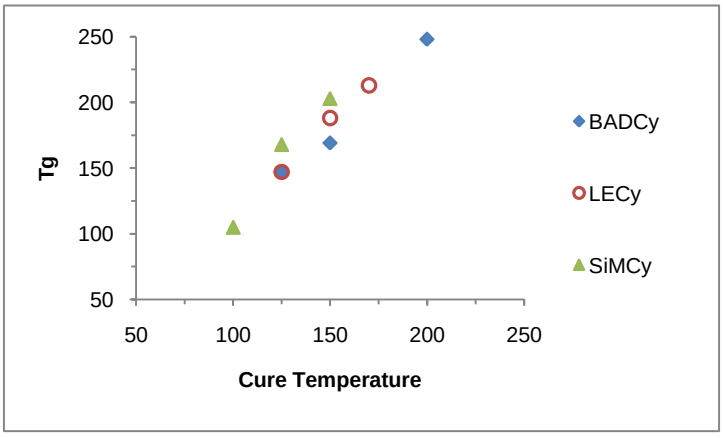


Figure 3. T_g determined from OTMA versus cure temperature for partially cured cyanate esters.

A careful examination of Figure 3 shows that though there is a clear correlation between the cured T_g and the cure temperature, the difference between the two is not constant, (as might be expected from simple considerations of vitrification), but continues to increase with increasing conversion. It is also worth noting that, based on the observed trends, the cure temperature and cured T_g appear to coincide at conversions of around 50-60%, or at the gel point during cure.

3.2 Effect of Moisture

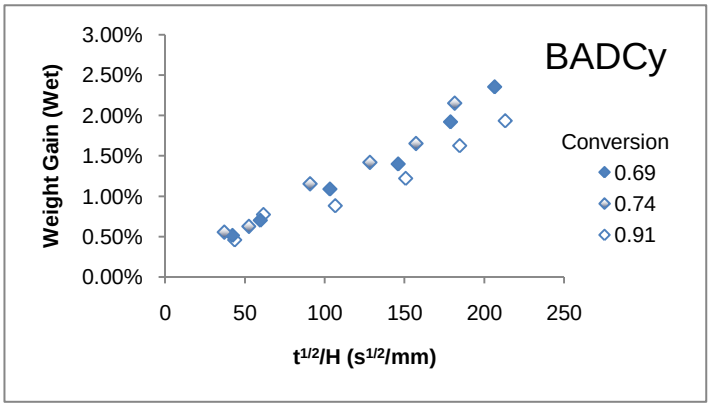
Cyanate esters with different extents of cure were immersed in water at 85°C and the weight gain of the samples was recorded at different time intervals. Table 3 shows the relative weight gain of partially cured BADCy, SiMCy and LECy after 96 hours submersed in water. Samples with a higher extent of cure had a lower weight percent water gain after 96 hours. All samples gained between 1.85 and 2.58 percent water with the exception of SiMCy cured at 100°C for 12 hours which showed a water gain of 4.53 percent.

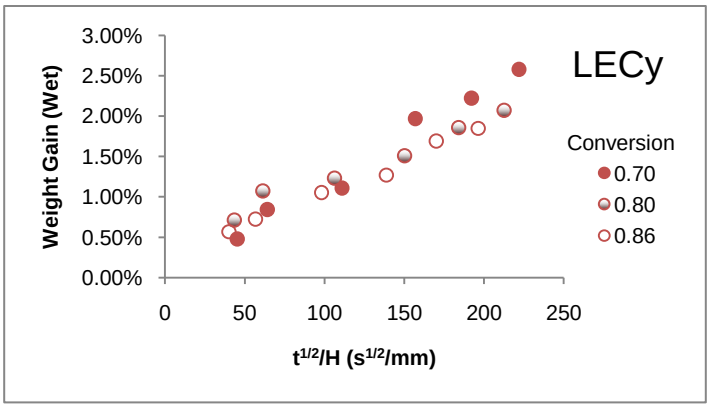
Table 3. Weight gain and TMA of cyanate esters after 96 hour water boil

Sample ID	Weight Gain (%)	Thickness (mm)
BADCy 125	2.35	2.85
BADCy 150	2.15	3.24
BADCy 200	1.93	2.76
LECy 125	2.58	2.65
LECy 150	2.07	2.77
LECy 170	1.85	2.99
SiMCy 100	4.53	3.21
SiMCy 125	2.35	2.64
SiMCy 150	1.83	3.04

Plots of the water uptake versus $t^{1/2}/H$, in which the slope near the origin is related to the diffusion coefficient, are shown in Figure 4 for the three materials studied. As would be expected for networks of similar chemical composition, the diffusion coefficient for water appears similar for all three materials. At later times, some trends begin to emerge. For LECy and SiMCy, there is a clear decrease in uptake with increasing conversion, while for BADCy the effect of conversion is less clear, although there does appear to be a general decrease with increasing conversion. Although as plotted, it is difficult to discern differences among the monomers, for fully cured samples it is clear that SiMCy does exhibit a lower water uptake compared to BADCy and LECy [23,24].

The water uptake behavior of uncatalyzed and catalyzed BADCy as a function of conversion has been reported by Georjon and Galy [11]. It was found that an increase in the degree of cure was accompanied by an increase in water absorption. This effect was attributed to an experimentally determined increase in free volume with increasing conversion. Samples with more free volume displayed higher water adsorption. In contrast, the materials in this study showed a decrease in water uptake with increasing conversion. However, this study covered a conversion range of around 0.6 – 0.9, whereas the work of Georjon and Galy covered a different conversion range of 0.85 – 1. Thus, the results do not necessarily conflict. In fact, for samples in which the T_g is less than, equal to, or only slightly higher than the exposure temperature, one would expect to see a significant increase in water uptake as the quantity $(T - T_g)$ decreases, reflecting the effects of plasticization. In fact, for the SiMCy sample cured at 100 °C, for which the measured dry T_g values ranged from 90 – 105 °C, it seems plausible that plasticization by hot water would eventually drive the T_g below the exposure temperature, resulting in a large increase in water uptake, just as was observed experimentally.





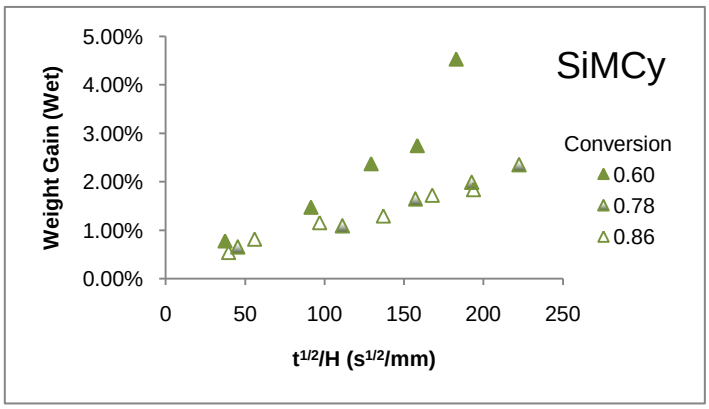


Figure 4. Plots of percent weight gain versus $t^{1/2}/H$ for BADCy, LECy and SiMCy with different extents of cure.

As a final point for discussion, it should be noted that the degree of cure of the materials studied was controlled by the cure temperature with cure times remaining constant. The degree of cure for polycyanurates studied previously has often been controlled by both changes in cure temperature and cure time. Polycyanurates with identical conversion but made from different cure schedules may have different three dimensional network architectures. Consequently, these materials may have different free volume fractions, average free volume hole sizes, free volume distributions and water uptake behavior even though the amount of unreacted cyanate groups is identical. Experiments comparing the free volume and water adsorption of materials with identical conversions prepared by low cure temperatures and long cure times versus those prepared by high cure temperatures and short cure times are thus needed to address this issue.

4. CONCLUSIONS

The cure characteristics and corresponding physical properties of three highly similar bisphenol dicyanate ester monomers over conversions ranging from around 0.6 to 0.9 have been examined. For all three monomers, the extent of cure, or conversion, showed a very strong dependence on the final cure temperature coupled with a very modest dependence on cure time. However, the cure temperature required to achieve a given level of conversion varied significantly, exhibiting a positive correlation with the rigidity of the dicyanate monomer. Somewhat counter-intuitively, because of the relative ease of cure of the more flexible monomers, the highest glass transition temperatures for a given cure temperature were often achieved with the most flexible monomers exhibiting the lowest fully cured T_g value. Although a strong positive correlation also existed between the final cure temperature and the glass transition temperature of the partly cured samples, the difference between cured T_g and cure temperature did not remain constant, but gradually increased, with cured T_g exceeding the cure temperature more and more as conversion beyond the gel point proceeded. Studies of moisture uptake showed similar diffusion coefficients for all three monomers at all levels of conversion studied, but at longer exposure times revealed a generally decreasing trend of total water uptake with increasing conversion over the conversion range studied (0.6 – 0.9), with the most significant changes taking place in samples with dry T_g values close to the exposure temperature.

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